Effect of honeycomb supporting on activity of $LaBO_{3\pm\delta}$ perovskite-like catalysts for methane flameless combustion

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Abstract

The activity of honeycomb supported $LaBO_{3\pm\delta}$ (B = Fe, Mn and Co) and La_2NiO_4 was tested for the catalytic flameless combustion (CFC) of methane and compared with their catalytic behaviour in powder form. Catalyst supporting brought about some modifications, mainly the complete loss of the suprafacial activity. Furthermore, thermal resistance of supported samples was checked through accelerated deactivation tests and showed to strongly depend on the nature of the B ion. Structural and morphological properties of fresh and aged catalysts, both in powder form (either pure or mixed with the primer precursor) and as honeycomb-supported samples, were compared to investigate the effect of each step of the dip-coating procedure. This allowed to shed light on the causes of the structural and chemical changes occurring during the wash-coating and leading to more or less severe decrease of performance and of thermal resistance of the final catalyst.
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1. Introduction

The abatement of gaseous pollutants such as NO_x, CO and unburnt hydrocarbons is of ever-growing concern for environment protection. Perovskite-like mixed oxides proved since long time to be a valuable alternative to the traditional noble metal based catalysts for many of these reactions, being cheaper, comparatively active and thermally stable, if properly prepared [1,2]. In particular, $LaBO_3$ (B = Mn, Co, Fe and Ni) perovskites showed high catalytic activity for the full oxidation of hydrocarbons [3]. Usually, the B ion is considered the main responsible of catalytic activity, while the La^{3+} cation imparts stability to the structure. However, doping at A position with cations of different valence contributes to the formation of oxygen vacancies and/or to the partial reduction or oxidation of the B ion and hence it can deeply affect catalytic activity [4].

For practical application, structured catalysts are the most used, in order to reduce substantially the pressure drop along the catalyst bed and to increase thermal stability of the active phase. Usually, structured catalysts are prepared by deposition of the active phase on cordieritic honeycomb monoliths. In order to favour the adhesion of the active phase to the support, the latter is usually pre-coated with a primer, whose function is also to increase the surface area and to improve catalyst durability [5]. One of the most commonly used primer materials is γ-Al_2O_3, which however in some cases does not ensure a sufficient stability. The latter can be improved either by doping alumina or by using different mixed oxides, such as Zr–Ce–Ti–Mg–O [6,7].

In a previous work [8], it was shown that $La_{0.9}Ce_{0.1}CoO_{3\pm\delta}$ could not be firmly anchored onto a honeycomb monolith in the absence of a primer. Furthermore, γ-alumina did not ensure enough thermal resistance to supported $LaBO_3$, due to the formation of different aluminates at high temperature, progressively leading to the destruction of the active phase during catalyst use. Moreover, γ-alumina itself sinters more or less rapidly, so reducing catalyst surface area. Finally, its different thermal dilation coefficient with respect to the cordieritic support and to the active phase layer can cause cracking and exfoliation of the coating. An alternative primer, ensuring a better thermal stability for the present application can be La_2O_3, especially when deposited from lanthanum nitrate as precursor [8,9].

The aim of the present work was to check the activity of honeycomb supported $LaBO_{3\pm\delta}$ (B = Fe, Mn and Co) and La_2NiO_4 for the catalytic flameless combustion (CFC) of

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methane and to compare their performance with that of the unsupported catalysts. For this purpose, several honeycomb-supported samples were prepared, in which the honeycomb was pre-coated with a La_2O_3 primer from nitrate. Structural and morphological properties of both the unsupported mixed oxide powder (either pure or mixed with the primer precursor) and of the supported catalysts have been analysed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Finally, the catalytic activity and thermal stability of the samples have been tested for the CFC of methane, before and after several reaction/accelerated deactivation cycles.

2. Experimental

2.1. Active phase preparation

Samples of $LaBO_{3\pm\delta}$ (B = Fe, Mn and Co) and of La_2NiO_4 were prepared by the flame hydrolysis (FH) technique, as reported elsewhere [3,10]. Briefly, a 3 wt.% aqueous solution of precursors ($La(NO_3)_3\cdot6H_2O$, Aldrich, purity $\geq 99.99\%$; $Mn(NO_3)_2\cdot4H_2O$, Riedel-de Haen, purity 97%; $Ni(Ac)_2\cdot4H_2O$, 4H_2O, Merck, purity 99.7%; $Fe(NO_3)_3\cdot9H_2O$, Merck, purity $\geq 99\%$; $Co(NO_3)_2$, Merck, purity $\geq 99.99\%$) was used. Citric acid (Aldrich, purity $\geq 99\%$) was added both as complexing agent and as additional fuel, to increase flame temperature. The solution was nebulised into a $H_2 + O_2$ flame and the perovskite-like powder was collected by means of 10 kV electrostatic precipitator.

Powder samples of La_2O_3 primer were obtained by calcination of La nitrate in air at 500 °C for 1 h. The lanthanum hydroxy-nitrate so obtained [9] was carefully grounded in agate mortar together with the catalyst powder in the ratio adopted for the preparation of supported samples (Table 1, samples prefix "P"). The mixture so obtained was calcined in air at 600 °C for 24 h and at 800 °C for 3 h.

2.2. Preparation of supported catalysts

For the wash-coating deposition of the primer, a clear and stable 10^{-4} M solution was prepared by dissolving $La(NO_3)_3\cdot6H_2O$ in distilled water. This concentration of lanthanum in the solution allowed to load up to 4 wt.% of primer on the dried monolith in a single dip-coating operation.

A detailed description of the apparatus and the conditions adopted for the dip-coating can be found elsewhere [8]. Briefly, a cylindrical 400 cpi cordierite honeycomb, 1 cm diameter × 5 cm length, was calcined at 500 °C for 1 h and weighed. The dip-coating was accomplished by means of a home made apparatus, so to dip and withdraw the honeycomb from the solution/suspension at the desired constant speed. The samples were then calcined at 500 °C in air for 1 h and weighed again. The deposition of the active phase was carried out by wash-coating the primer-coated monolith with a suspension of the perovskite powder. The latter was obtained by ball-milling 0.8 g of the FH prepared catalysts in 20 cm³ of a 0.4 vol.% solution of nitric acid for 4 h. Finally, the samples were calcined at 500 °C for 1 h and further weighed.

Primer and active phase loading was expressed as weight percent referred to the final catalyst mass. The composition of the supported catalysts is given in Table 1 (samples prefix "H").

2.3. Catalyst characterisation

X-ray diffraction analysis was carried out by means of a Philips PW 1820 diffractometer, using the Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). Phase recognition was made by comparison with literature data [11]. A Cambridge Stereoscan 150 scanning electron microscope was employed for morphological analysis.

2.4. Catalytic activity

Catalytic activity tests for the CFC of methane were carried out by means of a bench-scale continuous Incoloy 800 tubular reactor (400 mm in length, i.d. 10.5 mm), put within two heavy metal blocks into an electric furnace. The honeycomb was placed in the isothermal middle part of the reactor, between two flocks of quartz wool. The void part of the reactor tube, above and below the catalyst, was filled with 10–20 mesh quartz beads. Prior to each run, the catalyst was activated in flowing air (20 cm³/min), while increasing temperature by 10 °C/min up to 600 °C, then kept for 1 h. The activity tests were carried out by feeding a mixture composed of 0.5 vol.% CH_4, 49.5 vol.% He and 50 vol.% air, while increasing temperature by 2 °C/min from 250 °C up to 600 °C. The outlet gas was analysed in-line by means of a HP 5890 gas chromatograph. The total flow rate of the gas mixture was calculated by referring to the mass of active phase, so to have an identical value of time factor ($\tau = W/F = 2.5$ mg of perovskite × min/cm³ of overall gas flow rate) for every test. In any of the activity runs, no trace of either CO or of partially unburnt carbonaceous residua was ever noticed.

2.5. Accelerated thermal deactivation tests

Accelerated thermal deactivation tests were carried out after keeping the sample at the temperature (T_f) of CH_4 full conversion, for 24 h. Then cycles of reaction/deactivation were accomplished by increasing temperature by 10 °C/min up to 800 °C, kept for 1 h. Temperature was then lowered to T_f, kept for 1 h, during which the catalytic activity was measured. The deactivation cycle was repeated three times.

Table 1
Catalyst composition and temperature for 50% methane conversion ($T_{1/2}$)

Sample	La_2O_3 (wt.%)	Active phase (wt.%)	$T_{1/2}$ (°C)
P-LaFeO₃-5	4.0	5.0	–
P-LaFeO₃-2	4.0	2.0	–
P-LaMnO₃	4.0	2.0	–
P-La₂NiO₄	4.0	2.0	–
P-LaCoO₃	4.0	2.0	–
H-LaFeO₃-5	3.5	5.4	487
H-LaFeO₃-2	3.9	2.0	478
H-LaMnO₃	3.4	2.1	477
H-La₂NiO₄	4.0	3.0	522
H-LaCoO₃	3.5	2.0	459

Comparison data for $T_{1/2}$ of powder samples are reported in ref. [3].

3. Results and discussion

3.1. Catalyst preparation

The active phase, prepared by FH, consisted of 20–60 nm spherical particles of the given composition (Table 1), usually with high perovskite-like phase purity and BET specific surface area (SSA) around 20 m^2/g. The Ni containing sample showed a compact structure, including a perovskite-like layer (general formula ABO_3) intergrown with a layer with "rock salt" arrangement (general formula AO). This confirms that the formation of Ni^{3+}, to be inserted in a perovskite-like lattice, is rather difficult, the Ni^{2+} oxidation state being very stable.

3.2. Catalytic activity

The results of the activity tests of the honeycomb-supported samples are reported in Fig. 1. All but one of the present catalysts showed quite active, allowing to completely convert methane at $T \leq 600$ °C. The worst catalyst showed $H-La_2NiO_4$, which at the same temperature allowed ca. 92% methane conversion only. Although the T_f values of the Mn-, Co- and Fe-based samples were similar, a noticeable difference could be observed for the temperature of half-conversion ($T_{1/2}$, Table 1). Indeed, H-LaCoO$_3$ showed more active than H-LaFeO$_3$-2 and H-LaMnO$_3$ catalysts, whose conversion curves overlapped almost perfectly.

In a previous work [8], it was shown that the best active phase loading of $La_{0.9}Ce_{0.1}CoO_{3\pm\delta}$ was 2 wt.%. Hence, a further sample with LaFeO$_3$ loading of 5 wt.% was prepared for comparison. No significant effect was observed on T_f, while a noticeable increase of $T_{1/2}$ was observed when increasing the loading from 2 wt.% to 5 wt.% (Table 1 and Fig. 1, samples H-LaFeO$_3$-2 and H-LaFeO$_3$-5).

When comparing the activity of the present honeycomb-supported samples with that of the same catalysts in powder form [3], the same activity scale was observed, the Ni-based sample remaining the less active and the Co-based catalyst being the best-performing one. However, supporting on honeycomb proved more detrimental for $H-La_2NiO_4$, which did not attain a full CH$_4$ conversion even at 600 °C, in contrast
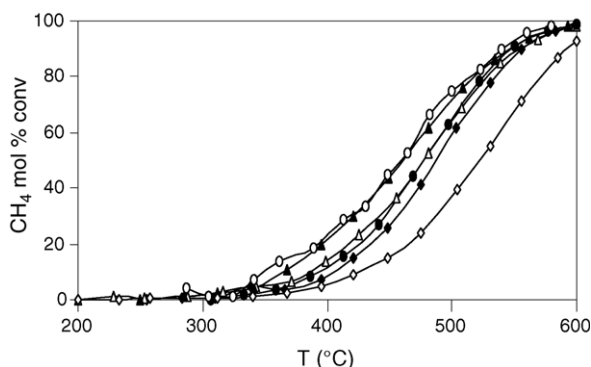
to what observed for the same sample in powder form. Furthermore, all of the present supported catalyst act almost exclusively through the intrafacial reaction mechanism, while for the powder LaFeO$_3$ and LaMnO$_3$ samples, an important contribution of suprafacial reactivity was observed [3], leading to ca. 30% and ca. 15% CH$_4$ conversion below 400 °C, respectively. Therefore, it can be concluded that supporting on honeycomb not only can strongly affect the formation of oxygen vacancies and hence the suprafacial activity, which may be even virtually suppressed, but also oxygen mobility, and hence intrafacial activity, i.e. the catalytic activity at high-temperature, as in the case of the Ni-based sample.

3.3. Thermal stability

The results of the deactivation tests on the present honeycomb-supported samples are reported in Fig. 2. H-LaFeO$_3$-2 showed the most stable sample, its activity dropping to 85% CH$_4$ conversion during the first deactivation cycle and then remaining constant up to the third cycle. A similar behaviour was observed with H-LaMnO$_3$, which however did not reach a plateau conversion after the repeated deactivation cycles. The worst behaviour was shown once again by the $H-La_2NiO_4$ sample, which showed a slight activity loss (from 92% to 89%) even after 24 h on-stream at T_f and a drop to less than 75% after the three deactivation cycles. By comparing the thermal resistance of the Fe-based samples with different perovskite loading, it is evident that a higher loading is detrimental also from this point of view.

The comparison of the present H-LaCoO$_3$ catalyst with $La_{0.9}Ce_{0.1}CoO_{3\pm\delta}$, which showed a final 5% decrease of methane conversion only, even after several deactivation cycles [8,9], allows to conclude that Ce doping is beneficial not only for activity, favouring oxygen mobility during the reaction, but also for thermal stability, due to the well-known properties of Ce as oxygen buffer [1,2].

To shed light on the causes of the more or less severe decrease of performance of the present samples after high-temperature ageing, morphological SEM analyses were carried out on the supported catalysts after the third deactivation cycle (Fig. 3). One may see that the poor thermal stability of the H-LaFeO$_3$-5 sample can be ascribed to the formation of deep
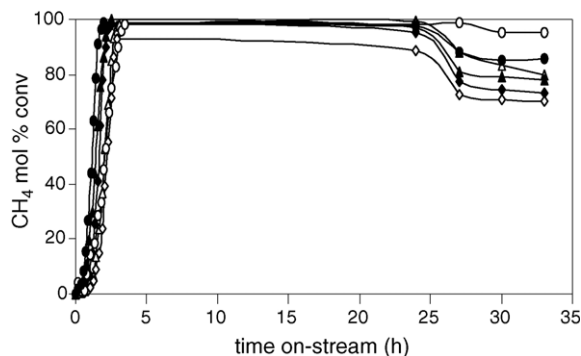

Fig. 1. Activity test of honeycomb-supported samples for the CFC of methane. $\tau = W/F = 2.5$ mg$_{cat} \times$ min/cm^3 of overall gas flow rate; feeding gas mixture: 20 cm^3/min of 0.5 vol.% CH$_4$, 49.5 vol.% He and 50 vol.% air: (○) H-La$_{0.9}$Ce$_{0.1}$CoO$_3$ (data from ref. [8,9]); (▲) H-LaCoO$_3$; (◆) H-LaFeO$_3$-5; (△) H-LaMnO$_3$; (◇) H-La$_2$NiO$_4$; (●) H-LaFeO$_3$-2.

Fig. 2. Thermal stability test data for the catalysts: (○) H-La$_{0.9}$Ce$_{0.1}$CoO$_3$ (data from ref. [8,9]); (▲) H-LaCoO$_3$; (◆) H-LaFeO$_3$-5; (△) H-LaMnO$_3$; (◇) H-La$_2$NiO$_4$; (●) H-LaFeO$_3$-2.
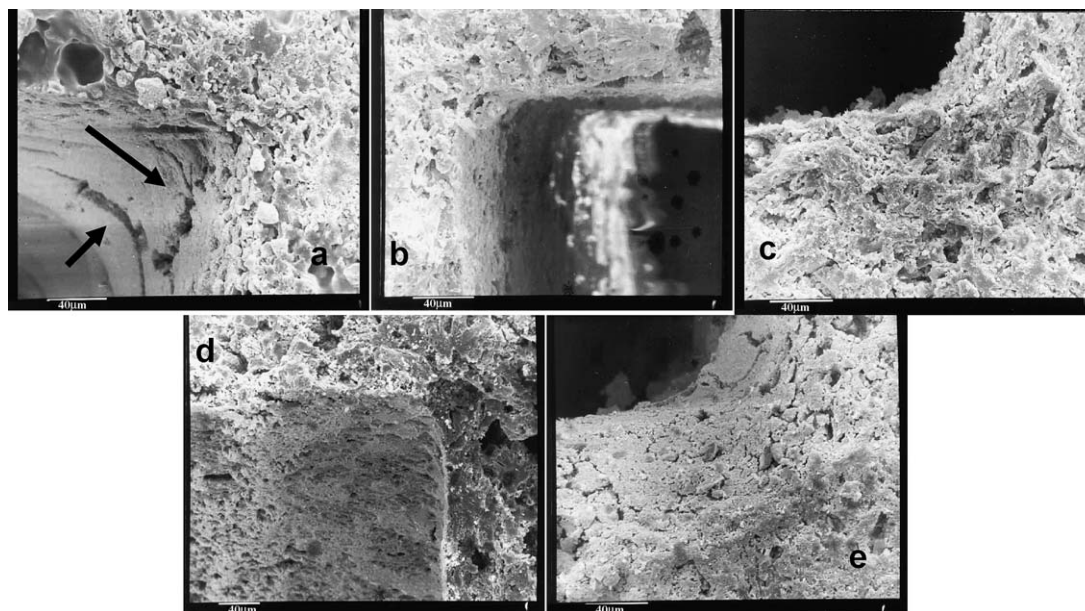
Fig. 3. Typical SEM micrographs of H-LaFeO$_3$-5 (a), H-LaFeO$_3$-2 (b), H-LaCoO$_3$ (c), H-LaMnO$_3$ (d) and H-La$_2$NiO$_4$ (e) after thermal deactivation tests.

cracks in the perovskite layer (Fig. 3a), due to the excessive oxide loading, followed by partial exfoliation of the active phase, as confirmed by the more or less abundant deposition of catalyst powder on the quartz wool supporting the honeycomb. No similar conclusion can be drawn for the other samples, whose SEM micrographs evidenced a compact perovskite layer (Fig. 3(b–d)). Some lower uniformity was observed for H-La$_2$NiO$_4$ (Fig. 3e), anyway not comparable to sample H-LaFeO$_3$-5, whose surface coating was by far more strongly affected by high-temperature treatments (Fig. 3a). However, mechanical reasons alone cannot suffice to explain the low activity and stability of the Ni-based sample, nor to justify the different resistance of samples H-LaFeO$_3$-2, H-LaCoO$_3$ and H-LaMnO$_3$. Hence, the possible effects of the dip-coating operations on catalyst structure were further investigated as follows.

3.4. Catalyst stability during honeycomb supporting

In our previous investigation [8], we compared catalytic activity and thermal stability of samples supported by means of different primer materials. In particular, we found that alumina works less satisfactorily as primer for supporting perovskites on cordieritic honeycombs, due to the different thermal dilation coefficient, which leads first to the formation of deep cracks in the coating layers and then to the exfoliation of the active phase upon heating at high temperature. Moreover, for Co-containing perovskites, an additional factor is the formation of cobalt aluminates and, more in general, of La aluminates of spinel-like structure when La-based perovskites are used. Both these undesired side effects lead to the partial destruction of the perovskite-like phase and hence to the decrease of catalytic activity.

With La$_2$O$_3$ as primer these problems could be largely avoided. In particular, satisfactory results were achieved by using La nitrate as precursor, calcined at 500 °C. At such a temperature, this precursor decomposes into a mixture of La hydroxy-nitrates, which favour the homogeneous dispersion of the active phase. Upon treatment at higher temperature, i.e. during the accelerated thermal deactivation tests, La hydroxy-nitrates transform into a compact layer of La$_2$O$_3$, firmly anchoring the perovskite to the support [9].

To investigate the chemical or physical modifications of the active phase during deposition on the support, a series of analyses have now been carried out after simulation of each step of the dip-coating procedure on the powdered precursors. The first step is the preparation of a stable water suspension of the perovskite powder, achieved by ball-milling for 2 h at room temperature and in the presence of diluted nitric acid as peptiser and milling aid. The results of the XRD analysis of the powder so recovered and dried are reported in Fig. 4.

The LaFeO$_3$ and LaMnO$_3$ samples (Fig. 4(a and c)) showed highly stable during the mechanical treatment in acid solution. Indeed, no substantial modification of the diffraction patterns was observed when comparing the as-prepared catalysts with the ball-milled homologues. By contrast, a decrease of crystallinity was observed for LaCoO$_3$ and especially for La$_2$NiO$_4$ samples (Fig. 4(b and d)). For both samples, the formation of surface hydroxyl groups was observed. Indeed, the incipient formation of La(OH)$_2$(NO$_3$) phase [11, file 23-1147] was recognised with sample LaCoO$_3$ (Fig. 4b), while sample La$_2$NiO$_4$ (Fig. 4d) partially transformed into LaNiO$_{2.7}$ [11, file 37-0928] and/or LaNiO$_3$ [11, file 34-1028]. The formation of some LaOOH [11, file 13-0436] was also observed after treatment of La$_2$NiO$_4$. The formation of hydroxy or hydroxy-nitrate species of La seems not to be particularly critical for activity and mainly for thermal stability. Indeed, the same behaviour was observed also for the highly active and resistant La$_{0.9}$Ce$_{0.1}$CoO$_{3\pm\delta}$ sample [8,9]. Conversely, phase transformation upon mechanical and acid treatment of La$_2$NiO$_4$ confirms its low phase stability, possibly affecting catalytic performance.
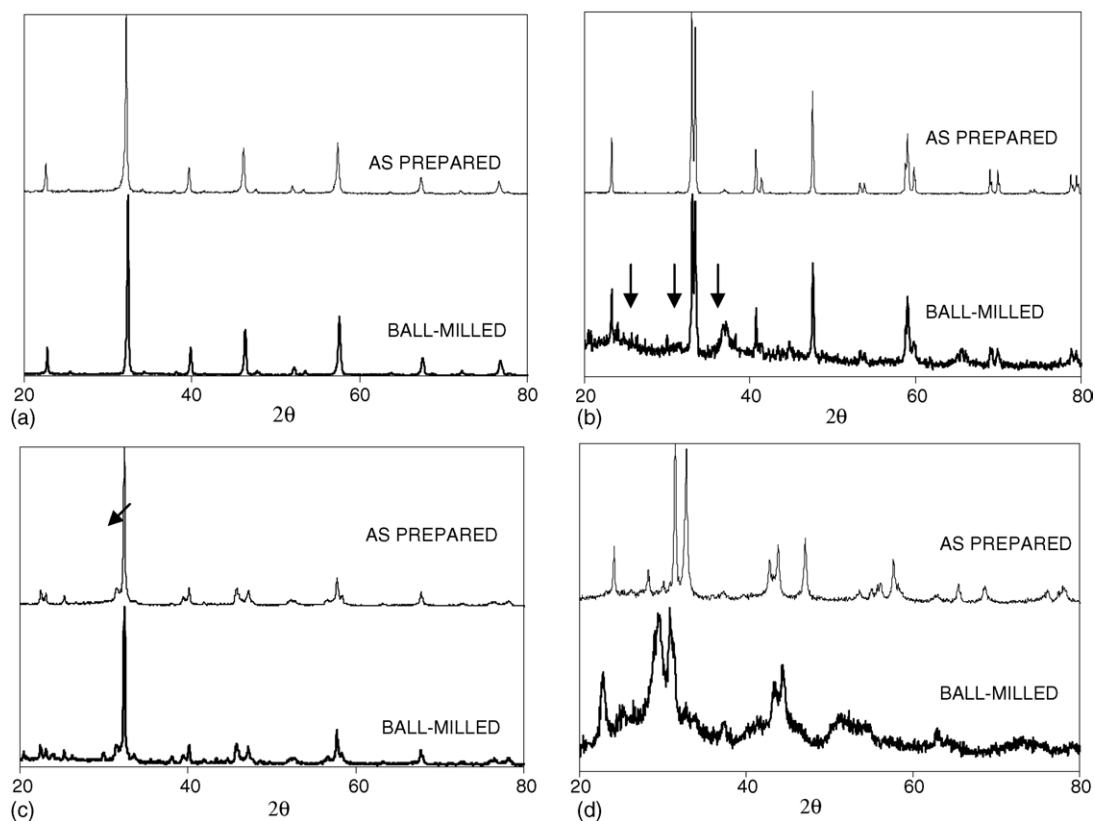
Fig. 4. XRD patterns of LaFeO$_3$ (a), LaCoO$_3$ (b), LaMnO$_3$ (c) and La$_2$NiO$_4$ (d) before (upper line) and after (lower line) the ball-milling procedure. Arrows indicate the occurrence of a phase other than perovskite.
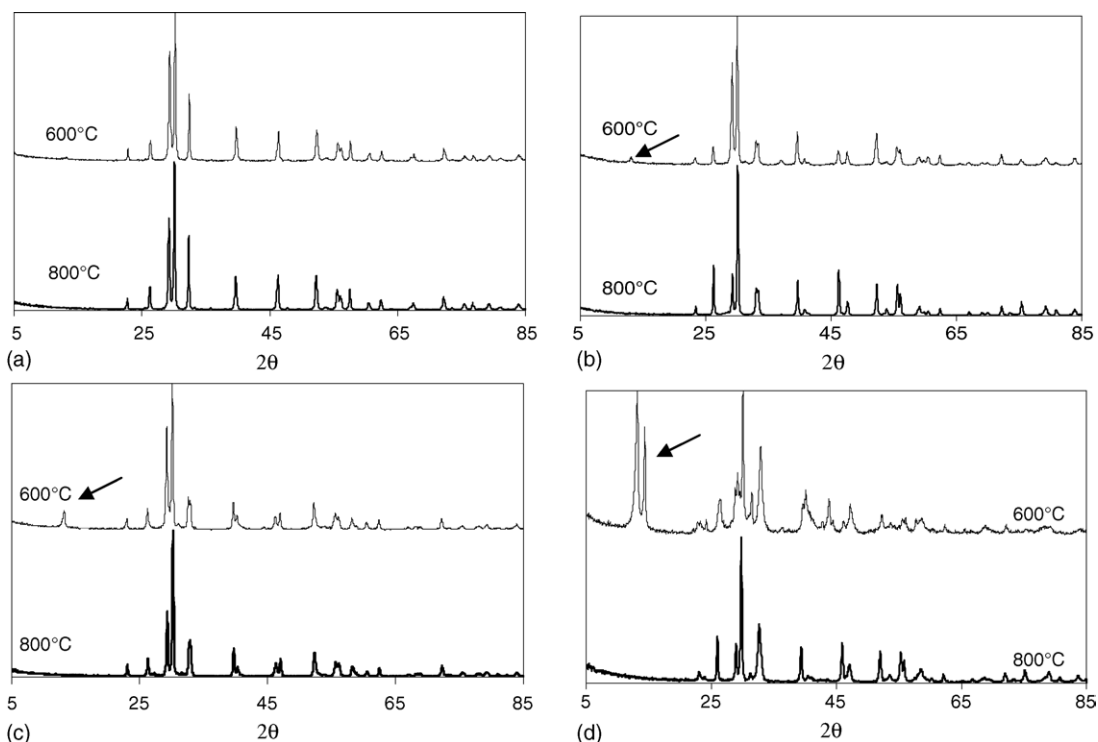

Fig. 5. XRD patterns of LaFeO$_3$ (a), LaCoO$_3$ (b), LaMnO$_3$ (c) and La$_2$NiO$_4$ (d) mixed with La hydroxy-nitrate and calcined at 600 °C (upper line) and 800 °C (lower line). Arrows likely indicate the presence of some La hydroxy-nitrate compound.

Indeed, the activity of this sample is predominantly intrafacial, hence depending on the redox properties of Ni and on oxygen mobility. The phase impurities introduced during this step of the dip-coating procedure may negatively affect at least the latter property. The other three supported samples kept a catalytic behaviour similar to that of the powder form. Hence, the moderate loss of crystallinity observed for the Co-based sample seems not fundamental from this point of view. The loss of suprafacial activity seems likely connected with the surface modification of the sample due to acid treatment, but this does not affect considerably the overall catalytic performance, which is mainly due to the intrafacial activity.

The ball-milled powder samples were then carefully mixed with the primer powder by hand milling in agate mortar and the mixtures so obtained were calcined in air at 600 °C and 800 °C. XRD analysis of samples P-LaFeO$_3$-2, P-LaCoO$_3$, P-LaMnO$_3$ and P-La$_2$NiO$_4$, (Fig. 5(a–d), respectively) evidenced some interaction between the primer precursor and the active phase. The most stable perovskite appeared to be LaFeO$_3$ (Fig. 5a), which showed two distinct phases (La$_2$O$_3$ and LaFeO$_3$) after both thermal treatments. A similar behaviour was observed for samples LaCoO$_3$ and LaMnO$_3$ (Fig. 5(b and c)), which substantially kept their structural arrangement after mixing with lanthanum oxide precursor and heating at 600 °C and 800 °C. By contrast, the structure of the Ni-based sample was strongly modified (Fig. 5d), with formation of hardly identifiable species after calcination at 600 °C, which transform into La$_2$O$_3$ + LaNiO$_3$ at 800 °C. This further confirms that the catalytic behaviour of the present Fe-, Mn- and Co-based supported samples, which generally reproduce the conversion of the unsupported catalysts, is substantially connected with the preservation of the original active phase. By contrast, the strong decrease of catalytic activity of the Ni-based sample is due to the deep phase modification occurring even after calcination at 600 °C only, i.e. under conditions similar to those of activation.

An exact attribution of a peak at $2\theta = 13°$ in some of the XRD patterns (Fig. 5) by comparison with the available literature data [11], was not possible. However, it can be very likely attributed to some La hydroxy-nitrate compound. Indeed, it appeared only after the addition of the lanthanum-based primer and completely disappeared upon calcination at 800 °C [9]. It is worth noting the substantial lacking of this species for LaFeO$_3$ (Fig. 5a), while its intensity progressively grew when passing to LaCoO$_3$ (Fig. 5b), LaMnO$_3$ (Fig. 5c) and La$_2$NiO$_4$ (Fig. 5d), in line with the progressive decrease of catalyst thermal stability (Fig. 2). This would suggest a mutual influence of the perovskite phase components on the stability of the final La$_2$O$_3$ + active phase system, the easier the formation of this hydroxy-nitrate phase, the lower the stability of the final catalyst.

4. Conclusions

The activity of the present honeycomb-supported catalysts showed generally similar to that of the corresponding unsupported samples. The loss of suprafacial activity is likely due to surface modifications during the ball-milling step of the dip-coating procedure. The Ni-based sample showed in any case the less active catalyst, due to deeper structural modifications occurring during the honeycomb supporting, through interaction with the La-based primer. A lower thermal stability of the supported samples seems to be connected with the easier formation of some hydroxy-nitrate species during the ball-milling preparation step in the presence of nitric acid as peptising milling aid and as stabiliser of the active phase/primer suspension. Finally, an excessive perovskite loading is detrimental for both activity and thermal stability.

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